

#### JP,2001-026894,A

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# **CLAIMS**

# [Claim(s)]

[Claim 1]A disposal method of salts containing a heavy metal being the method of impressing direct current voltage to inter-electrode [ which was provided into fused salt containing a heavy metal ], and depositing a heavy metal in the negative pole, maintaining at a temperature requirement more than the melting point of a heavy metal which deposits temperature of said fused salt, and separating a depositing heavy metal and salts by a molten state.

[Claim 2]A disposal method of salts containing the heavy metal according to claim 1 separating individually a heavy metal which increased impressed electromotive force gradually, electrolyzed for every impressed electromotive force, and deposited by electrolysis of each stage.

[Claim 3]A disposal method of salts containing the heavy metal according to claim 1 or 2 being within the limits whose temperature of fused salt containing a heavy metal is 500 \*\* - 1100 \*\*.

[Claim 4]A processing unit of salts containing a heavy metal having a cell characterized by comprising the following.

The anode and the negative pole.

A DC power unit which impresses direct current voltage among these two poles. A stirring means.

[Claim 5]A processing unit of salts containing the heavy metal according to claim 4 being what a stirring means depends on composition with which a rolling mechanism was provided in an electrode inserted in a cell.

[Claim 6]A processing unit of salts which contain in a wall of a cell the heavy metal

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the treatment technique which removes and detoxicates a heavy metal from the salts containing a heavy metal.

[0002]

[Description of the Prior Art]Although many of incineration residues generated when a municipal solid waste, industrial waste, etc. are incinerated are used for land reclamation, the reduction has been demanded as reservation of a reclaimed ground becomes difficult. Since harmful heavy metals, such as lead and cadmium, are contained in the ashes (incineration fly ash) which dispersed from the incinerator among incineration residues and were caught with the dust catcher, processing which detoxicates a heavy metal must be carried out on the occasion of the disposal. For this reason, processing which fuses an incineration residue is performed as a method that reduction of an incineration residue and detoxication can be performed simultaneously in recent years.

[0003]As treatment technique which fuses this incineration residue, there is the method of using the melting furnace of an electrical resistance type and the melting furnace of an induction heating method. For example, in the method of using the melting furnace of an electrical resistance type, the melt of the incineration residue is made to stagnate in a furnace, and melting of the incineration residue is inserted in and carried out on it, energizing and heating to this melt. Under the present circumstances, since salts, such as sodium chloride, potassium chloride, and a calcium chloride, are contained in incineration fly ash so much, while the above mentioned melt is stagnating in a furnace, that ingredient dissociates and the layer of molten slag and the layer of fused salt generate according to specific gravity difference. And when discharging melt, judgment discharge of fused salt and molten slag is performed.

[0004] Thus, among the discharged melts, after being solidified, molten slag is used as aggregate etc. or is used for land reclamation. However, since the heavy metal contained in incineration fly ash is contained in fused salt with the water-soluble gestalt, on the occasion of the disposal, detoxicating treatment must be carried out again.

[0005] There is a method indicated to JP,60-61087, A as conventional technology which

performs detoxicating treatment of such salts. In this method, the salts discharged from the melting furnace are dissolved in water, and that solution is prepared. And after adding caustic alkali of sodium to this solution and making it alkalinity, a chelating agent is added, a small amount of heavy metals are also settled, and the sediment which filters this and contains a heavy metal is separated and removed. On the other hand, crystallization processing according [an intermediary] to cooling operation and evaporation operation is performed in the solution from which the heavy metal was removed, and extraction of the dissolved salts is performed.

[0006]In another treatment technique, after using as solution the salts discharged from the melting furnace, the removing method which electrolyzes this solution and deposits a heavy metal is shown.

[0007]

[Problem(s) to be Solved by the Invention]However, in the above-mentioned conventional technology, since water is added to the salts discharged from the melting furnace and it is made solution, a throughput increases and equipment becomes large-sized. Since the salts in solution must be taken out on the occasion of disposal of solution after removing a heavy metal, crystallization operation must be performed. For this reason, it is necessary to also have devices, such as a crystallizer and a filtration apparatus, and the whole equipment becomes very complicated. A lot of power and subsidiary materials are consumed.

[0008] This invention does not need to perform operation of making the quantity of the salts to process increasing, and an object of this invention is to provide the disposal method of the salts which can simplify the composition of a processing unit and containing a heavy metal.

[0009]

[Means for Solving the Problem] The above-mentioned technical problem is solved by the next invention.

[0010] The 1st invention is the method of impressing direct current voltage to inter-electrode [ which was provided into fused salt containing a heavy metal ], and depositing a heavy metal in the negative pole, It is a disposal method of salts containing a heavy metal maintaining temperature of said fused salt at a temperature requirement more than the melting point of a heavy metal to deposit, and separating a depositing heavy metal and salts by a molten state.

[0011]In this invention, since fused salt is electrolyzed in the state as it is and a heavy metal is removed, it does not increase in a throughput. For this reason, a processing unit is miniaturized. Since electrolytic treatment is only performed and a heavy metal

can be deposited, down stream processing is very simple. A depositing heavy metal is a molten state, and since a heavy metal and salts are separable according to specific gravity difference, a heavy metal and salts are separable by simple methods, such as two-layer separation by a sedimentation method.

[0012] The 2nd invention is a disposal method of salts containing a heavy metal separating individually a heavy metal which increased impressed electromotive force gradually, electrolyzed for every impressed electromotive force, and deposited by electrolysis of each stage in the 1st invention.

[0013]According to this invention, each heavy metal is independently separable from fused salt containing two or more heavy metals, respectively by increasing impressed electromotive force gradually and electrolyzing every impressed electromotive force. namely, " in the 1st-step electrolysis " impressed electromotive force " peculiar electrolytic potential " most " \*\* " electrolyzing by setting it as a value corresponding to electrolytic potential of a heavy metal " most " \*\* " a heavy metal is deposited and it dissociates from fused salt. subsequently, impressed electromotive force " peculiar electrolytic potential " the next " \*\* " it electrolyzes by using a value corresponding to electrolytic potential of a heavy metal, the heavy metal is deposited, and it dissociates from fused salt. henceforth, impressed electromotive force " one by one " peculiar electrolytic potential " \*\* " it electrolyzes by using a value corresponding to electrolytic potential of a heavy metal, and a depositing heavy metal is classified, respectively and are collected.

[0014] The 3rd invention is a disposal method of salts containing a heavy metal being within the limits whose temperature of fused salt containing a heavy metal is 500 \*\* - 1100 \*\* in the 1st invention or invention of the 2nd.

[0015] Fused salt discharged when a municipal-solid-waste incineration residue is fused is a mixture which mainly consists of chlorides, such as NaCl, KCl, and CaCl<sub>2</sub>, and the melting point is about 500-800 \*\*. Although heavy metals contained in the above-mentioned fused salt are copper, lead, cadmium, zinc, etc., a chloride of these heavy metals is about 300-600 \*\* in the melting point. The melting points of metal which deposits when this chloride is electrolyzed are about 300 \*\* · 1100 \*\*.

[0016]On the other hand, the boiling points of NaCl and KCl which are main salts, and CaCl<sub>2</sub> are about 1400 \*\* · not less than 1600 \*\*. For this reason, if fused salt is processed in a 500·1100 \*\* temperature requirement, both salts and a depositing heavy metal can be maintained at a molten state. Thus, since salts and a depositing heavy metal are maintained at a molten state, separation of a heavy metal and salts is easy.

[0017] The 4th invention is a processing unit of salts containing a heavy metal having

the anode and the negative pole, a DC power unit that impresses a direct current among these two poles, and the cell provided with a stirring means.

[0018]In this invention, since it has a stirring means, movement of a heavy metal ion is performed promptly and a deposit of a heavy metal is performed efficiently.

[0019] The 5th invention is a processing unit of salts containing a heavy metal being what a stirring means depends on composition with which a rolling mechanism was provided in an electrode inserted in a cell in the 4th invention.

[0020]In this invention, since an electrode also has a stirring function, it is not necessary to have a stirring means for exclusive use, and a cell is simplified.

[0021] The 6th invention is a processing unit of salts containing a heavy metal providing the negative pole in a wall of a cell in the 4th invention or invention of the 5th.

[0022]In this invention, since area of the negative pole can be substantially made large, a heavy metal can be deposited promptly and fused salt can be electrolyzed efficiently. [0023]

[Embodiment of the Invention] <u>Drawing 1</u> is drawing of longitudinal section of an outline showing an example concerning an embodiment of the invention. As for a cell and 11, in <u>drawing 1</u>, the anode and 12b of a DC power unit and 12a are the negative poles 10. The cell 10 has encapsulated type structure and the wall is formed with the carbon material which has corrosion resistance to fused salt. The electrodes 12a and 12b are also formed with the carbon material. The heating method 15 by an electric heating or induction heating is formed in the external wall surface, and the cell 10 can heat the fused salt in a tub, and can hold it now to prescribed temperature.

[0024]And the agitator 14 is formed in the cell 10 as a means to stir the salts in a tub. It may be a bubbling apparatus using non-oxidizing gases, such as nitrogen gas, as a stirring means. Among the figure, 13 are a septum, they surround the anode 12a, are arranged and are formed with the porous material which consists of ceramics etc. This septum 13 is formed in order for contact with the metal and the anode 12a which deposited by electrolysis to prevent a deposited metal from being ionized again. 30 show among a figure fused salt and the molten metal in which 31 deposited.

[0025]Processing of the fused salt by the device of the above-mentioned composition is performed as follows. Fused salt is inserted in from the fused salt feed hopper 16, and starting and stirring the agitator 14 if needed, fused salt is heated by the heating method 15, and it holds to the prescribed temperature within the limits of 500 \*\* - 1100 \*\*. Subsequently, electric supply is performed from DC power unit 11, and the direct current voltage corresponding to the electrode 12a and the electrolytic potential in which the heavy metal for removal deposits among 12b is impressed. By impression of

this direct current voltage, it moves toward the negative pole 12b, and on the surface of the negative pole 12b, \*\*\*\* ion serves as metal and deposits. Since the depositing heavy metal is a molten state, it sediments and collects on the pars basilaris ossis occipitalis of the cell 10.

[0026] After continuing electrolysis as mentioned above and reducing the heavy metal concentration in fused salt below to a predetermined value, the draw of fused salt is performed from the fused salt outlet 18. The depositing molten metal 31 is extracted from the metal outlet 19, receives in a mold, is used as an ingot, and is collected.

[0027]And since gaseous chlorine is emitted from the surface of the anode 12a like a following formula at the time of the above-mentioned electrolysis, exhaust gas is extracted, it sends to a flue gas treatment apparatus, and a caustic-alkali-of-sodium solution is made to absorb gaseous chlorine.

$$2Cl \cdot 2e \cdot > Cl_2** (1)$$

[0028] Drawing 2 is drawing of longitudinal section of an outline showing other examples concerning an embodiment of the invention. In drawing 2, about the portion concerning the same composition as drawing 1, the same numerals are attached and explanation is omitted. In this processing unit, the negative pole 12b inserted in the cell is constituted pivotable, and it also has the function which stirs fused salt. That is, it is connected to DC power unit 11, and the negative pole 12b has a pivotable structure by the motor 20. The heights by a rib etc. are provided in the negative pole 12b, and it is formed in the shape which has a function of stirring wings.

[0029]Furthermore drawing 3 starts an embodiment of the invention, it is drawing of longitudinal section of an outline showing other examples. In drawing 3, about the portion concerning the same composition as drawing 1, the same numerals are attached and explanation is omitted. In this processing unit, the wall of the cell 10 is connected to DC power unit 11, and the wall of the cell 10 has become the negative pole 12b. The negative pole 12b is formed in the perimeter or the particular part of the side-attachment-wall inner surface of the cell 10. Since the surface area of the negative pole in which a heavy metal deposits is dramatically large if this processing unit is used, a heavy metal can be deposited promptly. For this reason, fused salt can be electrolyzed efficiently.

[0030] If the material which forms the wall of the cell 10 provides the negative pole which becomes the whole surface or the particular part of an inner surface of the cell 10 from conductive materials, such as a carbon material, not conductive materials, such as a carbon material, but in being ceramics etc. for example, the same effect as the above can be acquired.

[0031]In the above-mentioned explanation, although description about the treating operation of the batch method which uses one set of a cell was performed, when the throughput of fused salt is abundant, the device which connected two or more sets of cells in series can be used, and processing which inserts in fused salt continuously can also be performed.

[0032]

[Example] (Example 1) The processing unit by the same composition as <u>drawing 3</u> is used, and the test result which performed detoxicating treatment of the salts containing a heavy metal is explained. When the salts with which this examination was presented carried out melting treatment of the incineration residue (burned ash and fly ash are mixed) of a municipal solid waste, they extracted the salts generated in the melting furnace. The analytical value of these salts is shown in Table 1. The main constituents of these salts are NaCl, KCl, and CaCl<sub>2</sub>.

Pb was contained as a heavy metal in which the restriction value based on a reclamation standard is established.

Zn was contained as heavy metals other than this.

[0033]

[Table 1]

[0034] The used cell was a product made from carbon, and was a cylindrical thing 150 mm in inside diameter. The electrode inserted a 10 mm carbon stick, used it as the anode, and used the wall of the cell as the negative pole.

[0035]About 3.0 kg of the above-mentioned salts were put into this cell, and melting was heated and carried out to 700 \*\* with the heater. And the seal of approval of the voltage of 2.0V is carried out among two poles, electrolytic treatment is carried out, and it was made for Pb and Zn to deposit together.

[0036]After performing electrolysis for 120 minutes on this condition, when the heavy metal which sedimented at the bottom of the cell was extracted, about 1.7g of mixtures which mainly consist of lead and zinc were collected. And when the elution test based on the Environment-Protection-Agency notification No. 13 was carried out about the salts from which the heavy metal was removed, the result was as being shown in Table 2. As shown in this table, the concentration of Pb is [ salts after processing ] less than the restriction value.

It was detoxicated to the state of meeting the reclamation standard.

Transition of Pb concentration in the fused salt which falls with progress of electrolytic treatment is shown in <u>drawing 4</u>.

[0037]

# [Table 2]

[0038](Example 2) In this examination, the stirring wings made from silica glass with which the cell was equipped were rotated at 200 rpm, and fused salt was stirred. Other conditions were made the same as Example 1. Transition of Pb concentration in the fused salt which falls with progress of the electrolytic treatment by this condition is shown in drawing 4. By this figure, in Example 2, compared with the example 1 case, the lowering speed of Pb concentration was large and the solvent wiping removal of Pb was efficiently performed for a short time so that clearly. Since a difference of the test condition of Example 2 and Example 1 is only the existence of stirring fused salt, it is clear the good result's by Example 2 to be brought by stirring fused salt during electrolysis.

[0039]And it was as being shown in Table 2, and like the case of Example 1, heavy metal concentration is less than the restriction value, and the result of having carried out the elution test based on the Environment-Protection-Agency notification No. 13 about salts after performing electrolytic treatment for 45 minutes was detoxicated to the state of meeting the reclamation standard.

# [0040]

[Effect of the Invention] The disposal method concerning this invention is a method of impressing direct current voltage to fused salt, and depositing a heavy metal.

Since fused salt is processed in the state as it is, a throughput does not increase and a processing unit is miniaturized.

And since temperature of fused salt is carried out on the occasion of this electrolysis more than the melting point of the heavy metal to deposit, the heavy metal and salts which deposited can be easily sedimented according to specific gravity difference.

[0041] The heavy metal which deposited by electrolysis of each stage is individually separable by increasing impressed electromotive force gradually and electrolyzing for every impressed electromotive force.

[0042] In the processing unit concerning this invention, by establishing a stirring means, movement of a heavy metal ion is performed promptly and a deposit of a heavy metal is performed efficiently.

[0043] When a rolling mechanism provides in an electrode, it is not necessary to have a stirring means for exclusive use, and a cell is simplified.

[0044] Area in which a heavy metal deposits can be substantially made large by providing the negative pole in the wall of a cell. For this reason, a heavy metal can be deposited promptly and fused salt can be electrolyzed efficiently.

[Brief Description of the Drawings]

[Drawing 1] It is drawing of longitudinal section of an outline showing an example concerning an embodiment of the invention.

[Drawing 2] It is drawing of longitudinal section of an outline showing other examples concerning an embodiment of the invention.

[Drawing 3] Furthermore it starts an embodiment of the invention, it is drawing of longitudinal section of an outline showing other examples.

[Drawing 4]It is a figure showing transition of Pb concentration which falls with progress of electrolytic treatment.

[Description of Notations]

10 Cell

11 DC power unit

12a Anode

12b Negative pole

13 Septum

14 Agitator

15 Heating method

16 Fused salt feed hopper

17 Exhaust gas outlet

18 Fused salt outlet

19 Metal outlet

20 Motor

30 Fused salt

31 Depositing molten metal

[Drawing 1]

[Drawing 2]

[Drawing 3]

[Drawing 4]